

Shape Transition of Magnetic Field Sensitive Polymer Gels

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ABSTRACT: Magnetic field sensitive gels, called ferrogels, are chemically cross-linked polymer networks swollen by a ferrofluid. The monodomain magnetic particles, with a typical size of about 10 nm, couple the shape of the polymer gel to the nonuniform external magnetic field. Shape distortion occurs instantaneously and disappears abruptly when an external magnetic field is applied or removed, respectively. This work provides a thermodynamic analysis of shape transition based on the free energy of the swollen network that includes the elasticity of network chains as well as magnetic interactions of finely dispersed solid particles with the external field. It is shown that noncontinuous shape transition is due to a shift of equilibrium state from one local minimum to another one, similar to a first-order phase transition. The discussions presented here may be useful for the design of magnetically active soft polymeric actuators.

I. Introduction

Polymer gels play an important role in many fields, for example in biotechnology, separation technology, and the cosmetic and pharmaceutical industries.^{1–3} Stimuli-responsive gels have recently been attracting a great deal of attention due to their ability to undergo large swelling degree changes in response to a small variation of the environmental conditions.^{3–8} Temperature, pH, and solvent composition are the most often used variables due to their importance in physiological and biological systems. These gels also offer opportunities for application in controlled drug delivery and uptake. On the other hand stimuli-responsive polymer networks have interest for use in soft actuators, micromanipulators, or artificial muscles. Attempts at developing stimuli-responsive gels are often complicated by the fact that structural changes such as shape and volume changes that occur are kinetically restricted by relative slow swelling or deswelling processes. This disadvantage often hinders the efforts of designing optimal gels for different applications.⁹ To accelerate the response time, magnetic field sensitive polymer gels have been developed.^{10–13} This new magnetocontrolled elastic medium, called ferrogel, is a chemically cross-linked polymer network swollen by a ferrofluid. A ferrofluid, or a magnetic fluid, is a colloidal dispersion of monodomain magnetic particles with a typical size of ~10 nm.^{14,15} In ferrogels the magnetic and high elastic properties are coupled. As a result significant shape distortion occurs instantaneously and disappears abruptly when an external magnetic field is applied or removed. This shape transition can be applicable to a variety of fields as a new driving mechanism.

In one of our previous work we have studied the unidirectional magneto-elasticity of ferrogels and observed continuous and abrupt (noncontinuous) shape distortion.^{13,17} The main objectives of this work are both to interpret these phenomena on the basis of thermodynamic arguments and to build an understanding of phenomena in order to offer an application oriented

inspiration. The knowledge on physical and chemical fundamentals of polymer containing magnetic field sensitive gels will play a role as guiding principles for possible technological applications as a new type of actuator material.

II. Theoretical Background

From the magnetic viewpoint the ferrogel is a dilute ensemble of noninteracting magnetic nanoparticles homogeneously distributed in the polymer network. Similar to the well-known magnetic behaviors of ferrofluids,^{14,15} above a certain temperature (the so-called mean blocking temperature), the ferrogel should show superparamagnetic characteristics. This means that the magnetization curve shows no hysteresis at all and can be fitted by a simple Langevin function corrected with the distribution of magnetic dipole moments. On the other hand the magnetization curve is temperature dependent (in the superparamagnetic temperature range) to the extent that curves taken at different temperatures, T , approximately superimpose when plotted against H/T , where H denotes the magnetic field strength.

In the absence of an external magnetic field a ferrogel presents a mechanical behavior very close to that of a swollen filler-loaded network. Since a typical magnetic gel can be considered as a dilute magnetic system we may neglect the influence of magnetic interactions on the modulus. Thus on the basis of rubber elasticity theory it is possible to express the elastic free energy density as a function of principal deformation ratios, λ_x , λ_y , and λ_z . These quantities are defined as the ratio of deformed and undeformed dimensions corresponding to the directions x , y , and z , respectively.

$$a_{el} = a_0 + \frac{1}{2} G(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3) \quad (1)$$

a_{el} represents the elastic part of the free energy density, G means the shear modulus and a_0 stands for the free energy density of the undeformed gel ($\lambda_x = \lambda_y = \lambda_z = 1$).

It is known that the elastic and swelling properties of gels cannot be satisfactorily described by the Gaussian network models. However, there are many experi-

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mental evidences showing that if the swelling degree exceeds a certain value, a virtual idealization of mechanical properties occurs. This ideal behavior means that for highly swollen networks—at least from a phenomenological point of view—the Gaussian model can provide an adequate description.¹⁶

III. Experimental Part

Preparation of Ferrogels. A magnetic field sensitive gel is a special type of filler-loaded gel, where the finely divided filler particles have strong magnetic properties. Preparation of a ferrogel does not require a special polymer or a special type of magnetic particles. As a polymer network, one may use every flexible chain molecule which can be cross-linked. The filler particles can be obtained from ferro- as well as ferrimagnetic materials.

Preparation of a ferrogel is similar to that of other elastomeric networks. One can precipitate well-dispersed particles in the polymeric material. The “in situ” precipitation can be made before, during, and after the cross-linking reaction.¹⁸ According to another method, the preparation and characterization of colloidal magnetic particles are made separately, and the cross-linking takes place after mixing the polymer solution and the magnetic sol are mixed together.¹⁹ In this paper, a chemically cross-linked poly(vinyl alcohol) hydrogel filled with magnetite particles is reported. At first, magnetite (Fe_3O_4) sol was prepared from FeCl_2 and FeCl_3 in aqueous solution. To counterbalance the van der Waals attraction and the attractive part of the magnetic dipole interactions, colloidal stability has been maintained by a small amount of HClO_4 , which induced peptization. Then the stabilized magnetite sol having a concentration of 10 wt % and an average particle diameter of 10 nm was mixed with poly(vinyl alcohol) solution. Poly(vinyl alcohol) (PVA) is a neutral water-swollen polymer which reacts under certain conditions with glutaraldehyde (GDA) resulting in chemical cross-linkages between PVA chains. The cross-linking density can be conveniently varied by the amount of GDA relative to the vinyl alcohol [VA] units of PVA chains. We have prepared weak PVA gels in order to allow the effect of magnetic interaction on deformation to develop as far as possible. The ratio of [VA] units to [GDA] molecules was varied between $100 \leq [\text{VA}]/[\text{GDA}] \leq 400$. A more detailed description of the chemical procedure can be found in our previous paper.¹⁰

Ferrogels of defined shape have been prepared. Cylindrical samples having a diameter of 1–2 cm and length of 10–20 cm were obtained. These gel tubes were used for the magnetoelastic investigations.

The ferrogels are characterized by the following symbols: sample name/polymer concentration (given in wt %) at which cross-links were introduced/the ratio of vinyl alcohol units to the cross-linking molecules/wt % of filler particles in the gel. For example a gel FG/6.3/300/4.25 means a ferrogel (FG) which was prepared at a polymer solution of 6.3 wt % of poly(vinyl alcohol), where the ratio of vinyl alcohol monomer units to the cross-linked molecules is 300 and the magnetite content at preparation is 4.25 wt %.

Magnetic Measurements. The static magnetization curves of different type of ferrogels have been determined at temperatures between 4 and 300 K. The measurements were carried out using a homemade vibrating sample magnetometer.

A small piece of ferrogel (put into a copper sample holder) was made uniformly vibrate in the air hole of a sensitive measure coil (1 cm long, 8000 turns of fine wires). The sample and the coil were both put into a He cryostat (Oxford Instruments, VT1 1.5–300 K) of which we were able to control the temperature between 4 and 300 K. This whole equipment was placed into a superconducting electromagnet (Oxford Instruments) being able to induce a well controllable, homogeneous magnetizing field up to 14 T with a high homogeneity on the order of 0.1 mT/cm. We measured the voltage induced in the measure coil in cases of different magnetizing field strength by a LOCK-IN amplifier (Stanford Research Systems,

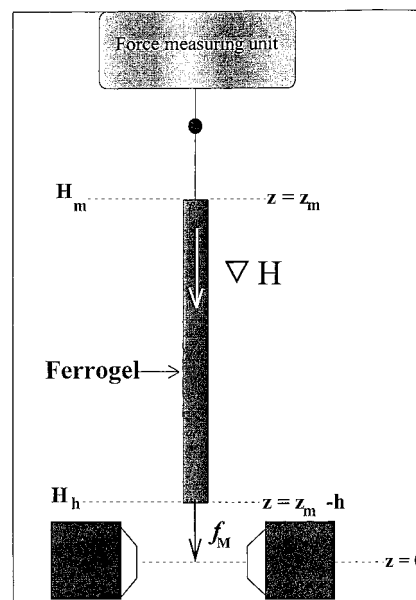


Figure 1. Schematic diagram of a ferrogel in nonuniform magnetic field.

SR830 DSP), which obtained the reference signal from the vibrating apparatus. This voltage was directly proportional to the magnetization of the sample.

Unidirectional Magnetoelastic Measurements. To study the elastic response of ferrogels to magnetic field, cylindrical gel tubes were suspended in water vertically between plan-parallel poles of an electromagnet. The position of the top surface of gels was fixed by a rigid copper thread at the position designated by z_m in Figure 1. The copper thread was connected to a force-measuring unit in order to establish the force developed in the ferrogel due to the interaction with magnetic field. The lower end of the suspended gel in the absence of external magnetic field is characterized by the position z_0 measured from the $z = 0$ line which corresponds to the axis at the face-to-face plan-parallel magnetic poles of the electromagnet. The magnetic field was induced by a steady current flowing through the electromagnets. This experimental set up allows us to treat the magnetoelastic coupling as a one-dimensional problem. We suppose that the magnetic field strength varies only in the z -direction; the possible variation to perpendicular directions (x and y) is neglected. The intensity of the current was varied between 0 and 10 A by an electronic power supply (FOK-GYEM TR-9177, Hungary) and the voltage was kept constant 40 V. The magnetic field vector, $\mathbf{B}(z)$ (sometimes called the magnetic induction or magnetic flux density) varies along the gel axis. It is worth to mention that B is proportional to the magnetic field strength, H ; that is $B = \mu_0 H$, where the proportionality factor, μ_0 , denotes the permeability of vacuum. B was measured along the z axis by a Teslometer (Phywe System GmbH, Germany) at different steady current intensities. The highest field strength between the poles of electromagnets we used was 840 mT. We have found that the z -directional distribution of magnetic field can be satisfactorily approximated by the following forms:

$$B(z) = B_{\max} f(z) \quad (2)$$

where B_{\max} represents the maximal magnetic induction at the position $z = 0$ and $f(z)$ is a unique function characterizing the experimental arrangement including the geometry of poles and the gap distance.

$$f(z) = 1 - kz^2 \quad \text{if } |z| < \delta \quad (3)$$

and

$$f(z) = (1 - k\delta^2) \exp[-\gamma(|z| - \delta)] \quad \text{if } |z| \geq \delta \quad (4)$$

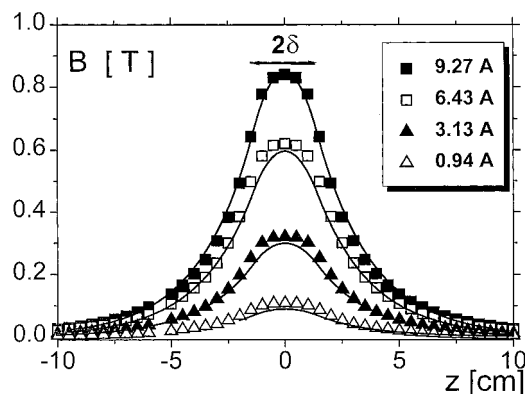


Figure 2. Dependence of the magnetic field strength on the distance measured along the z axis. The steady current intensities are indicated in the figure. The solid line represents the field calculated on the basis of eqs 2–5.

where γ is a characteristic constant describing the exponential decay of field strength at larger distances, δ means the radius of poles and the constant, k ($k = \gamma/(2\delta + \gamma\delta^2)$), was determined by considering the same slope of $f(z)$ functions at a distance $\gamma = \delta$, where the two functions (eqs 2 and 3) approach each other. According to the Biot–Savart law B_{\max} is determined by the steady current intensity, I , flowing through the electromagnets:

$$B_{\max} = k_1 I \quad (5)$$

where k_1 means a proportionality factor. It must be mentioned that the value of k_1 strongly depends on the quality of electromagnets. Figure 2 shows a comparison of experimental data and phenomenological description based on eqs 2–5.

To determine the elongation–stress dependence, experiments were monitored by a digital video system as shown in Figure 3. A CCD camera with a $1/3$ in. video chip has been connected to a PC through a real time video digitizer card. The movement of the end of gel cylinder was followed on the magnified picture by a homemade program, which has properly mixed the digitized picture coming from the video source with the computer screen image. By this method very short movements (one pixel on the screen) can be monitored and measured on the real time video image. The error of the measurement depends on the magnification; however, in our cases it was within 0.01 mm.

A magnetic field gradient was used to deform the gel. All the measurements were performed at room temperature.

IV. Experimental Results

Figure 4 shows a typical magnetization curve measured at room temperature. In reality we have measured more magnetization cycles in case of every

sample, but in order to make them easier to survey, only a few representative points have been plotted in the figure. According to our expectation (i.e. the ferrogel exhibits superparamagnetic characteristics, similarly to magnetic fluids) the hysteresis disappeared above approximately 50 K and the single-valued magnetization curves could be satisfactorily fitted by the Langevin function. In the figure, the solid line represents the Langevin function determined from the values of initial susceptibility and saturation magnetization. Since the magnetic gel is superparamagnetic above 50 K, the small nanosized particles distributed in the polymer matrix should also have superparamagnetic behavior (i.e., the magnetic moment can rotate inside the particle without rotation of the whole particle) since the magnetization does not show any differences between the frozen and unfrozen states. This also means that the ferrogel becomes polarized in an external magnetic field without rotation of the particles, so the polymer matrix is not locally deformed during the magnetizing process.

On the basis of experimental data we can conclude that, within the experimental accuracy, no hysteresis loop has been found. This means that the remanent magnetization of the ferrogel can be neglected. This finding is supported by other measurements performed on different ferrogels. This is an important result, which says that in a relative slowly (a few hertz) alternating magnetic field the transformation of magnetic into thermal energy is rather small. For this reason, devices made of ferrogels and subjected to alternating magnetic field—due to a narrow hysteresis loop—are characterized by small energy losses per cycle.

The sensitivity of ferrogel to the nonuniform magnetic field strongly depends on the magnetite concentration of the gel. To reach the largest possible sensitivity, one has to increase the amount of magnetic filler particles. However, the magnetite concentration of ferrogel has an effect on the elastic modulus as well. To find the optimal amount of magnetite, first we need to know the magnetic susceptibility–magnetite concentration dependence. In Figure 5 we plotted the susceptibility of some different types of ferrogels against its magnetite concentration. From the experimental data, we can conclude that magnetic susceptibility depends linearly on the amount of filled magnetite, expressed in volume fraction (Φ_m), and the proportionality factor is equal to 0.34.

Figure 6 shows the effect to a magnetic field on the deformation of ferrogel. The relative displacement is plotted against the steady current intensity. It can be

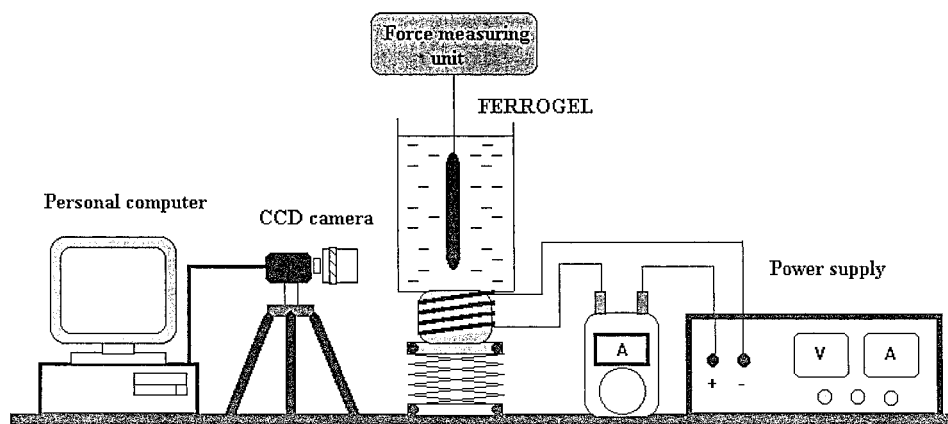


Figure 3. Schematic diagram of the experimental setup used to study the magnetoelastic properties of ferrogels.

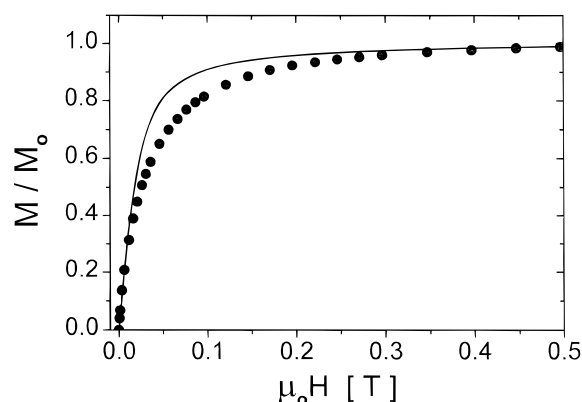


Figure 4. Magnetization of a ferrogel as a function of magnetizing field strength. The solid line represents the Langevin function fitted to measured points. The difference between the measured and fitted points is due to the size distribution of magnetic particles embedded in the polymer network.

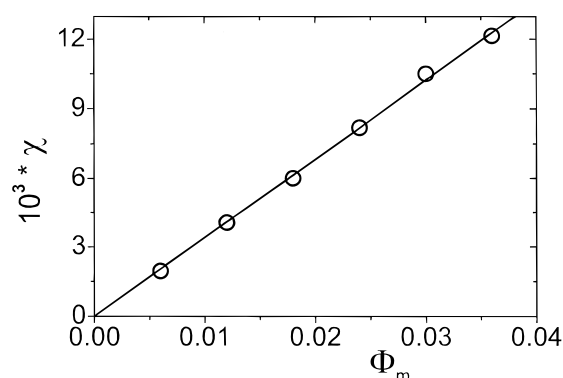


Figure 5. Initial magnetic susceptibilities of some ferrogels with different amount of magnetite particles. The measured points can be suitably fitted by a straight line in accordance with our expectations.

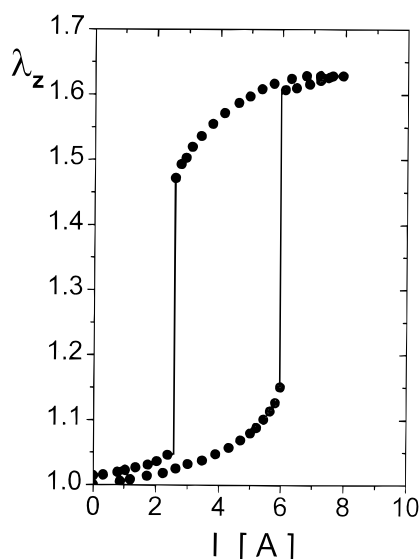


Figure 6. Noncontinuous deformation of ferrogel in an ordinary magnetic field. The deformation ratio is plotted against the intensity of current flowing through the electromagnet that induced the magnetic field.

seen that the displacement of the lower end of the ferrogel—due to the magnetic force—is rather significant. A giant magnetostriction takes place. In many cases we were able to produce an elongation of 40% of

the initial length by applying a nonuniform magnetic field. It may be seen that at small current intensities the displacement slightly increases. However, at a certain current intensity a comparatively large, abrupt elongation occurs. This noncontinuous change in the size appears within an infinitesimal change in the steady current intensity. Further increase in the current intensity results in another small extension.

We have found that by decreasing the current a contraction takes place. Similar to the extension, the contraction was found to have a noncontinuous dependence on current intensity. It is worth mentioning that the discrete shape transition occurred within a time interval of one tenth of a second, independent of the gel size.

The peculiar property of the ferrogel's magnetoelasticity is the hysteresis that characterizes the extension–contraction processes. Despite its irreversible nature, this process is time independent under ordinary conditions. It must be emphasized that the observed hysteresis phenomena is not a consequence of well-known magnetic hysteresis of ferromagnetic materials, since according to our measurements the ferrogels exhibit no magnetic hysteresis at all (see Figure 4).¹¹

By variation of the experimental conditions, we have found a crossover between continuous and discontinuous shape transitions.¹⁷ The initial position in the nonuniform magnetic field seems to play an essential role in the mode of stretching. The crossover between continuous and noncontinuous transitions seems to be determined by the initial position of the gel. A similar observation has been made for other ferrogels having a much smaller amount of magnetite. We have varied the magnetite concentration of ferrogels in wide range between 2.75 and 12.6 wt %. For all of the gels, similar abrupt shape transitions have been observed.

V. Interpretation of Experimental Results

General Consideration. From a thermodynamic viewpoint, the Helmholtz free energy contains the most important information regarding the stability of an isothermal, isochor system. The equilibrium shape of an object represents the free energy minimum. Any small distortion must result in a free energy increase. If an external stress is imposed, the free energy as a function of object shape is changed, so that the new minimum represents a displacement from the original equilibrium state. We consider here a magnetic field sensitive polymer gel at constant temperature and volume. We put the ferrogel into a nonuniform magnetic field and study the shape change (deformation) due to magnetic interactions. In this case, the free energy of magnetic field sensitive gel contains two terms, an elastic part and a magnetic part. The shape of the gel is characterized by the deformation ratios.

If we consider unidirectional deformation along the axis z ($\lambda_x = \lambda_y$) and take into account the constancy of volume $\lambda_x \lambda_y \lambda_z = 1$, then eq 1 can be rewritten as

$$a_{el}(\lambda_z) = a_0 + \frac{1}{2} G \left(\lambda_z^2 + \frac{2}{\lambda_z^2} - 3 \right) \quad (6)$$

In general, the deformation induced by the magnetic field cannot be considered as a homogeneous deformation (so λ_z depends on z) because the force density varies from point to point in space. However, a special dis-

tribution of the magnetic field can be found where the deviation from the homogeneous case is not significant.

The magnetic part of free energy density can be expressed as

$$da_M = BdM \quad (7)$$

here, M denotes the magnetization, and B stands for the magnetic induction. The magnetization is defined as the ratio of magnetic moment to the volume.

In practice the magnetization cannot be directly controlled, rather the magnetic field strength, B , applied to the sample can be varied. It is therefore useful to introduce the magnetic free energy function, which is a Legendre transform of a_M that replaces the magnetization by the magnetic field strength. This new function is defined as

$$a_B = a_M - BM \quad (8)$$

and

$$da_B = -MdB \quad (9)$$

To be able to integrate this equation we have to linearize the Langevin function, which describes the $M(B)$ dependence. However, it is to be remarked that this simplification is valid only up to about 50 mT, as seen in Figure 4. Therefore, the integration of both sides from zero to a finite value of magnetic field strength results in

$$a_B(B) = a_0 - \frac{\chi}{2\mu_0} B^2 \quad (10)$$

where a_0 denotes the free energy density of the unstrained ferrogel in the absence of magnetic field.

The overall free energy density of a ferrogel is the sum of a_{el} and a_B .

$$a(\lambda_z B) = a_0 + \frac{1}{2} G \left(\lambda_z^2 + \frac{2}{\lambda_z} - 3 \right) - \frac{\chi}{2\mu_0} B^2 \quad (11)$$

It is worth mentioning that the above equation includes two independent terms (elastic and magnetic). A cross term does not exist because not the individual particles, but their moments rotate during the magnetizing process. As a result, micromechanical interactions of the filler particles with the polymer matrix do not need to be considered.

The total free energy of a cylindrical gel, having a volume of V , and cross-sectional area d_s can be expressed as follows:

$$A[\lambda_z B(z)] = a_0 + \frac{1}{2} GV \left(\lambda_z^2 + \frac{2}{\lambda_z} - 3 \right) - \frac{\chi d_s}{2\mu_0} \int_{z_0}^{z_0+h} B^2(z) dz \quad (12)$$

where z_0 represents the position of the bottom end of the gel cylinder having a height of h . Thus $z_0 + h$ corresponds to the coordinate of the top surface of the gel cylinder. Both quantities, d_s and h , can be related to the deformation ratio, λ_z .

$$h = h_0 + \lambda_z \quad (13)$$

$$d_s = d_0 \lambda_z^{-1} \quad (14)$$

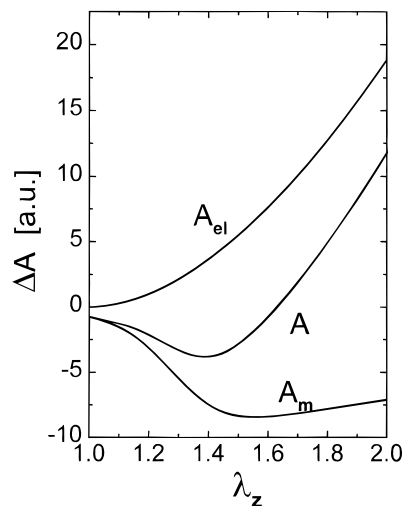


Figure 7. Magnetic and elastic parts and the total of the free energy calculated on the basis of eq 15.

Equation 14 takes into account that the cross-sectional area continuously decreases as the elongation increases. d_0 denotes the cross section of an undeformed gel cylinder. The value of integral in the right-hand of eq 12 strongly depends on the magnetic field distribution.

The overall free energy of a ferrogel, A , located in a nonhomogeneous magnetic field can be expressed as follows:

$$A[\lambda_z B(z)] = a_0 + \frac{1}{2} GV \left(\lambda_z^2 + \frac{2}{\lambda_z} - 3 \right) - \frac{\chi d_0}{2\mu_0 \lambda_z} \int_{z_0}^{z_0+h_0 \lambda_z} B^2(z) dz \quad (15)$$

At a given magnetic field distribution, $B(z)$, it is possible to calculate how the overall free energy depends on the strain for all possible configurations. Figure 7 shows the free energy change, ΔA , due to magnetoelastic interactions as a function of deformation ratio. For the numerical solution of eq 15 the magnetic field distribution given by eqs 2–4 was used. This figure presents not only the overall free energy, but also the elastic and magnetic contributions. It is seen that the elastic part of the free energy is a monotonic increasing function of the deformation ratio, whereas the magnetic contribution decreases at small deformation and begins to increase at higher strains. The reason of this nonmonotonic dependence is due to the constancy of the gel volume during deformation. In eq 15 the front factor of the integral keeps on decreasing as the gel becomes thinner and thinner during elongation. On the other hand, the value of integral keeps on increasing as a result of stretching. The product of these two terms varies with the deformation ratio in a nonmonotonic manner.

The Condition of Equilibrium. It follows from the basic principle of thermodynamics that the equilibrium state of a ferrogel is characterized by the minimum of the free energy with respect to the strain. It is therefore important to study the shape of the free energy function, $\Delta A(\lambda_z)$. The extremum principle implies both $d[\Delta A(\lambda_z)] = 0$ and that $d^2[\Delta A(\lambda_z)] > 0$. This latter condition determines the stability of the equilibrium states. We have systematically varied the steady current intensity and studied the shape of the $\Delta A(\lambda_z)$ dependence. These results are shown in Figure 8. It can be seen that at

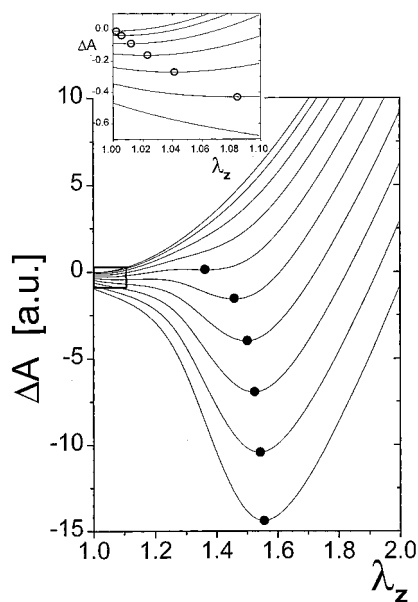


Figure 8. Total free energy plotted against the deformation ratio at different current intensities. The initial, framed part of the curves is enlarged and plotted on an additional plot as well. The local minima representing the equilibrium states are designated by open and solid circles, respectively. The current was varied between 1 A (top curve) and 10 A (bottom curve).

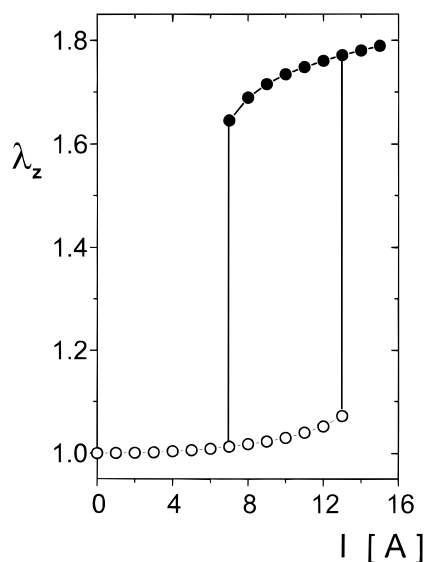


Figure 9. Results of model calculation based on the numerical solution of eq 15. The equilibrium points, which correspond to the minima of the free energy function are plotted against the current intensity. Open and solid circles represent forward and backward directions, respectively.

each current intensities a minimum point, denoted by open circle, can be found. At current intensities of $I < 5$ A the minima occur at small strains $\lambda_z < 1.05$. It is also seen that by increasing the current, the deformation ratio increases. When the positions of minimum points are compared, it is possible to establish the dependence of strain on the steady current intensity. This is shown in Figure 9. It was found that λ_z scales with the square of current intensity in accordance with our previous finding.¹²

When the steady current intensity $I > 5$ A is increased—as shown in Figure 8—we observe two minima. One is located at comparatively small strains; for the other one, a much deeper minimum can be found

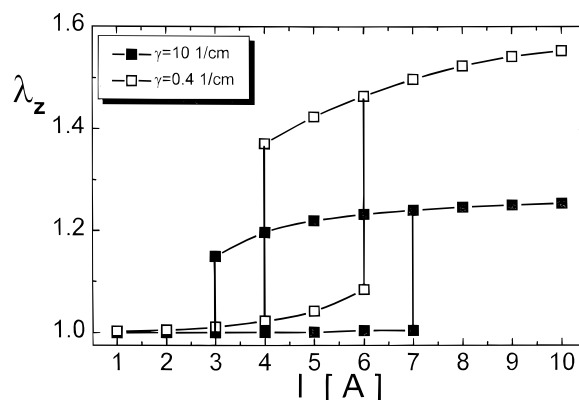


Figure 10. Influence of the magnetic field distribution on the shape of $\lambda_z - I$ dependence.

at significantly larger deformation ratio. Full circles in Figure 8 designate the second minimum. The energy gap between the two minima is rather shallow. Consider that the system is in the less stable minimum. After a certain time the fluctuations will carry this state into the stable deeper minimum. Since the probability of fluctuations falls very rapidly with the height of energy gap, so the fluctuation from the deeper minimum to the other one is very improbable. Thus the system remains in this deeper minimum, and this state is considered to be the stable state. On the basis of this figure it is possible to provide an understanding of the magnetoelastic hysteresis phenomenon. Let us decrease the current intensity. As a result the stable deeper minima shifts to a smaller deformation ratio. The fluctuation from here into the other minimum (open circle) is still impossible. We should decrease the current intensity far below the value at which the transition from primary minima to secondary minima occurs. When the height of the energy gap between the two minima becomes small enough, then the transition into the primary minimum will be possible. The significant difference of the current intensities corresponding to the transitions from the primary to secondary minima and the opposite direction manifests itself as a magnetoelastic hysteresis.

The Effect of Magnetic Field Distribution. We have systematically varied the range of magnetic field strength by changing the parameter γ . This corresponds to the variation of the magnetic field gradient, which is $\gamma B(z)$. Now the position of the minimum points is plotted against the steady current intensity. The results of two representative examples are shown in Figure 10. One can see that the field gradient makes its strong influence felt. With increasing γ , the height of the jump significantly decreases. This is an important result, which says the change of the value of γ makes the control of the measure of the noncontinuous shape transition possible, which is very desirable from the applications point of view.

Another important result says that the width of the hysteresis also depends on the magnetic field gradient. To obtain narrow hysteresis, it is better to choose a small γ , that is a magnetic field that does not change drastically in the direction of z .

It must be mentioned that we cannot decrease γ optionally in order to increase the measure of the deformation because below a critical value of γ noncontinuous, an abrupt shape transition does not exist. Further decrease of γ results in only negligible deformation. In this case the field can be considered to be

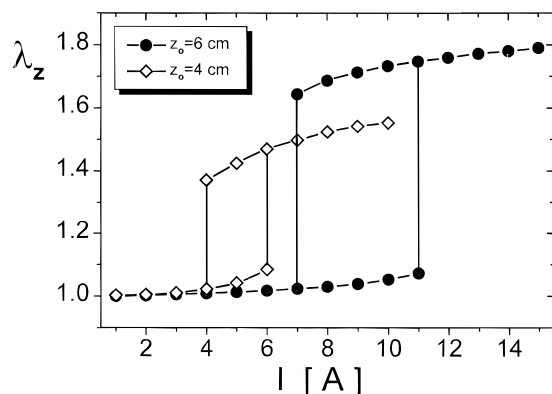


Figure 11. Effect of initial position on the hysteresis phenomena.

almost homogeneous. In a homogeneous field there is no force acting on the particles; therefore, the shape of the ferrogel remains the same.

The other way to vary the magnetic field gradient is to locate the gel into another position, that is to change the value of z_0 . When z_0 is increased, the effective magnetic field gradient decreases due to the smaller value of $B(z)$. As a result, we observe the same effect as in the case of smaller γ . Figure 11 shows the result of two representative examples. However, we have to mention that the more significant, noncontinuous deformation happens obviously at a higher current intensity if we increase z_0 , and this requires more energy. The only difference is that the width of the hysteresis does not increase when we decrease z_0 .

For technical applications, it is important to have a large displacement. On the basis of our calculation, we have concluded that the highest possible displacement comes into existence when γ is the smallest possible for an abrupt transition and the position of the gel corresponds to the maximum z_0 where abrupt elongation can still occur.

We have also studied the influence of the gap width, δ , between the poles of electromagnets. It was found that no significant effect comes into existence. It must be mentioned that within the interval $-\delta < z < \delta$. The magnetic field can be considered as homogeneous; therefore, no force develops, and no deformation occurs in this range.

The Influence of Magnetic Particle Concentration and Elasticity of the Gel. In the previous chapter we showed how strongly the distribution of the applied magnetic field influences the deformation of ferrogels. Therefore, in the cases of every conceivable and different kinds of ferrogel-based applications, we must precisely design the suitable magnetic field distribution that is able to induce the required motion of the gel. However, one more question arises in the design of gel-based machines, namely, the choice of the used ferrogel type. Fortunately it is possible to answer this question universally because all the applications require the very best ferrogel that can transform the magnetic energy into mechanical work with the highest possible efficiency.

There are two relevant constituents that influence the goodness of ferrogels and that can be conveniently varied during the preparation. The first is the magnetic particle concentration (denoted by Φ_m), which can be varied up to about 8 vol % and the second one is the elastic modulus of the ferrogel (G_0), which can be varied

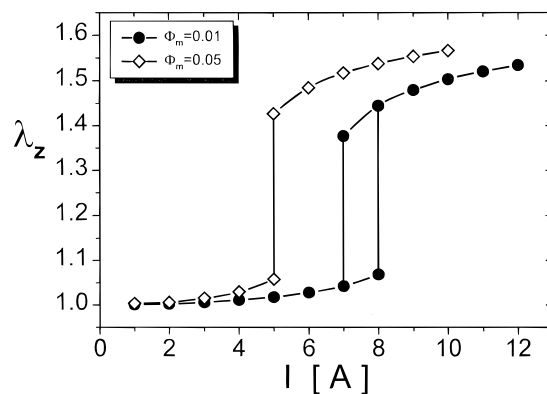


Figure 12. Deformation ratio plotted against the steady current intensity for gels having different amounts of magnetic particles.

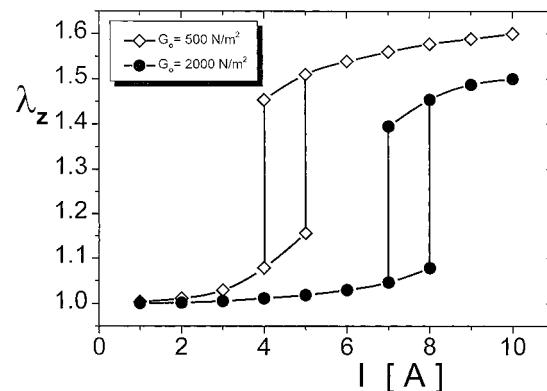


Figure 13. Influence of cross-linking density (expressed in terms of g_0) on the $\lambda_z - I$ dependence.

in a wide range by the amount of cross-linking agent. Let us see first the effect of the magnetic particle concentration. We expect that the gel being more magnetic is more easily deformable because the magnetic force acting on the gel is greater. Figure 12 shows the calculated deformation of two different ferrogels at the same geometry and magnetic field. The gels differ only in the magnetite content. It is seen that the deformation degree is nearly the same in both cases. The only difference is that the noncontinuous transition (i.e. the jump) happens at 5 A in the case of the gel with a higher amount of magnetite and at 8 A in the other case. It means that by making an increase in the amount of magnetic particles in the gel, we can increase its sensitivity; that is to say we need less energy to reach the same deformation. However, despite the increase of the magnetic force with an increase in the magnetite concentration, we cannot reach a larger deformation. The reason for this is that the small nanoparticles distributed in the polymer network create new cross-links between polymer chains and the gel become less elastic. The increase of the magnetic force strength is counterbalanced by this additional increase of the elastic force. To eliminate this disadvantage, we should decrease the number of cross-links in the gel by decreasing the GDA amount. The effect of the change of elasticity on the magnetic field induced deformation is shown in Figure 13. On the basis of the figure we can conclude that a decrease in the GDA amount is advantageous from two viewpoints. First of all, the ferrogel jumps at a smaller current intensity, and second, it jumps larger. However, there is a lower limit of decrease in the GDA amount because GDA is needed to stabilize the polymer

network with the creation of chemical bonds between the chains. Consequently, if we want to prepare the ideal ferrogel for applications, we have to increase its magnetic concentration to as high a value as possible and we have to decrease its GDA contents to as low as possible.

VI. Future Aspects

The ability of magnetic field sensitive gels to undergo a quick controllable change of shape can be used to create an artificially designed system possessing sensor and actuator functions internally in the gel itself. The peculiar magnetoelastic properties may be used to create a wide range of motion and to control the shape change and movement, which are smooth and gentle similar to those observed in a muscle. Thus, application of magnetic field sensitive gels as a soft actuator for robots and other devices has special interest. Unlike in metallic machine systems, devices made of gels work without noise, heat evolution, and exhaustion. An understanding of magnetoelastic coupling in gels will hasten the gel engineering to switches, sensors, micro-machines, active vibration control, and biomimetic energy-transducing devices

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References and Notes

- (1) Peppas, N. A.; Korsmeyer, R. W., Eds. *Hydrogels in Medicine and Pharmacology*; CRC Press: Boca Raton, FL, 1987.
- (2) De Rossi, X.; Kawana, K.; Osada, Y.; Yamauchi, A., Eds. *Polymer Gels, Fundamentals and Biomedical Applications*; Plenum Press: New York, London, 1991.
- (3) Harland, R. S.; Prud'homme, R. K. *Polyelectrolyte Gels*; ACS Symposium Series 480; American Chemical Society: Washington, DC, 1992.
- (4) Tanaka, T. *Science* **1982**, *218*, 467.
- (5) Tanaka, T. *Phys. Rev. Lett.* **1978**, *40*, 820.
- (6) Osada, Y. *Adv. Polym. Sci.* **1987**, *82*, 1.
- (7) Osada, Y.; Okuzaki, H.; Gong, J. P. *Trends Polym. Sci.* **1994**, *2*, 2.
- (8) Hoffman, A. S. *Macromol. Symp.* **1995**, *98*, 645.
- (9) Suzuki, A. *Adv. Polym. Sci.* **1993**, *110*, 199.
- (10) Zrínyi, M.; Barsi, L.; Büki, A. *Polym. Gels Networks* **1997**, *5*, 415.
- (11) Barsi, L.; Büki, A.; Szabó, D.; Zrínyi, M. *Prog. Colloid Polym. Sci.* **1996**, *102*, 57.
- (12) Zrínyi, M.; Barsi, L.; Büki, A. *J. Chem. Phys.* **1996**, *104*, 20.
- (13) Zrínyi, M. *Trends Polym. Sci.* **1997**, *5*, 277.
- (14) Berkovski, B.; Bashtovoy, V., Eds. *Magnetic Fluids and Applications Handbook*; Begell House, Inc.: New York, Wallingford, CT, 1996.
- (15) Rosenweig, R. E. *Ferrohydrodynamics*; Cambridge University Press: Cambridge, England, 1985.
- (16) Mark, J. E.; Erman, B. *Rubberlike elasticity—A molecular Primer*; Wiley & Sons: New York, 1988.
- (17) Zrínyi, M.; Barsi, L.; Szabó, D.; Kilian, H. G. *J. Chem. Phys.* **1997**, *106*, 5685.
- (18) Mark, J. E. *Br. Polym. J.* **1985**, *17*, 144.
- (19) Haas, W.; Zrínyi, M.; Kilian, H. G.; Heise, B. *Colloid Polym. Sci.* **1993**, *271*, 1024.

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